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BY S. DUSHMAN

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COPPER ANODES IN CHLORIDE SOLUTIONS.

By Saul Dushman.

In the following paper I intend to give a summary of an investigation undertaken with the object of explaining the anomalous behavior of copper as anode in chloride solutions. Preliminary experiments showed that copper dissolved with a valency ranging from 1 to 2, according to the experimental conditions. It was observed that in concentrated hydrochloric acid solution, it dissolved as a univalent metal, while in more dilute solution the valency was greater, and finally attained a value of 2 for very dilute solutions. The particular concentration of hydrochloric acid at which the copper ceased to dissolve as purely univalent varied with the rate of stirring, rate of circulation, current density, and other factors. Increased stirring or circulation caused the metal to dissolve much more as cuprous, while increasing the current density, under otherwise constant conditions, increased the proportion of cupric.

Although several hypotheses could have been made to explain these experiments, the one chosen seems to be in best accord with the quantitative experiments described below. It is assumed that the copper anode dissolves by the action of the current in such a manner that, at the boundary between solution and electrode, the chemical equilibrium between the cupric and cuprous salts in hydrochloric acid solution is maintained.

The investigation therefore naturally divided itself into two parts: (a) Investigation of the chemical equilibrium, (b) determination of concentrations at the electrode in the electrolytic experiments. The chemical equilibrium between cuprous and cupric salts has been investigated by E. Abel,[1] R. Luther,[2] and Bodländer and Storebeck.[3] A large number of experiments performed by myself, in which the methods of analysis and manipulation were different from any of the above, proved in conformity with those of the last named authors. The equilibrium between copper, cupric and cuprous salts in presence of hydrochloric acid is represented by two equations:

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[1] E. Abel, Zeit. f. Anorg. Chem., **26**, 361.

[2] R. Luther, Zeit. f. Physik. Chem., **36**, 385.

$$\overset{\circ}{\mathrm{Cu}} + \ddot{\mathrm{Cu}} \rightleftharpoons 2\,\dot{\mathrm{Cu}} \tag{1}$$

$$\dot{\mathrm{Cu}} + 2\,\acute{\mathrm{Cl}} \rightleftharpoons \mathrm{Cu}\,\acute{\mathrm{Cl}}_2 \tag{2}$$

Bodländer and Storbeck determined the values of the constants $k_1 = (\ddot{\mathrm{Cu}})/(\dot{\mathrm{Cu}})^2$ and $k_2 = (\mathrm{Cu}\acute{\mathrm{Cl}}_2)/(\dot{\mathrm{Cu}})(\acute{\mathrm{Cl}})^2$ as 1.4×10^4 and 4×10^4, respectively, concentrations being in mols per litre.

The second part of the investigation had for its object the determination of the concentration at the anode during the electrolytic experiments, so that the values of k_1 and k_2 might be calculated from these and compared with those obtained from the equilibrium experiment. Fig. 1 is a diagram of the electrolytic cell used. It consisted of two porous cylinders, P_1 and P_2, between the ebonite discs, E E, two concentric glass cylinders, L and M, also held between ebonite discs, and a rotating copper anode, A, making contact with a shaft and holder, H. To prevent liquid from entering within the anode tube, two ebonite plugs (the lower of these having a glass Tip, T) were provided with threaded holes, so that they could be tightened against the copper, as shown in the diagram. The tube could therefore be taken off the plugs and weighed. Its area was about 40 square centimetres. A rubber tube, with stopper, S, fitted over the upper plug. The electrolyte entering B passed between the two porous cylinders, through holes in the center disc, E, and the glass cylinder, M, and up and around the anode, leaving by means of the exit tube, D. The cathode consisted of a platinum gauze, C, attached around the discs E. The different parts were cemented together. Cork wedges between the discs and the glass container, F, prevented any lateral motion of the discs when the anode was set rotating.

Since hydrochloric acid containing air in solution dissolves

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[3] G. Bodländer and Storbeck, Zeit. f. Anorg. Chem., 31, 1. 45

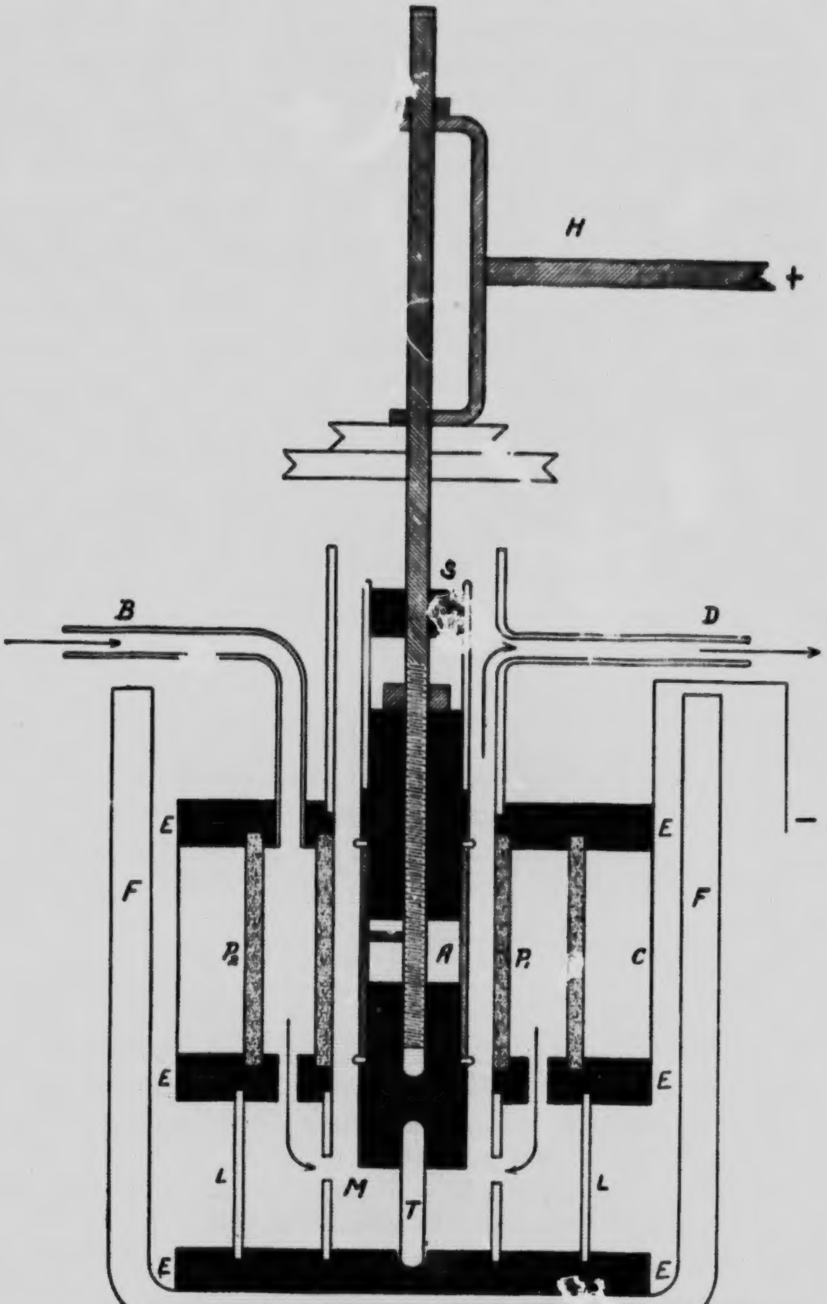

FIG. 1.

copper even without current, the solution to be electrolyzed was always freed from air by exhaustion, and then saturated with carbon dioxide. Blank experiments showed that in such a solution the copper dissolved only very slightly. A large bottle filled with stock solution was permanently connected with a carbon dioxide generator, and as the solution ran out into the cell, the gas took its place. After circulating through a cell once, the electrolyte passed into a measuring cylinder, and was then discarded. A copper coulometer and ammeter were placed in series with the cell. During the experiment, the rates of circulation and stirring were kept nearly constant, the average speed of rotation being about 1,500 per minute in all the experiments.

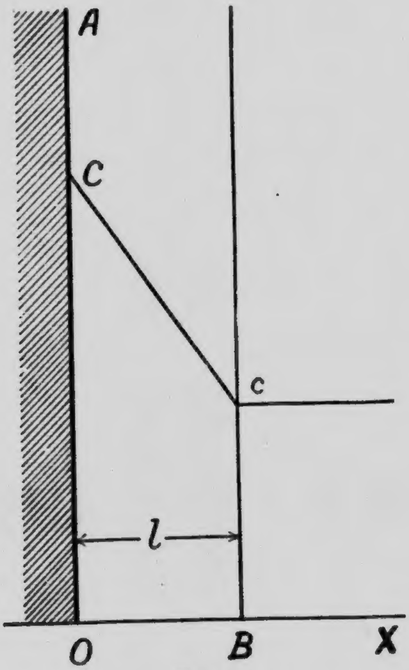

FIG. 2.

Now we shall consider how, by means of such an arrangement, we can calculate, in a simple manner, the concentrations at the electrode, for these are evidently different from those in the solution at a distance from the electrode.

In Fig. 2, let OA represent a section of the electrode, whose area is S. Let OX represent the distance from the electrode. It has been shown by Nernst and Brunner that in a rapidly stirred solution the diffusion is limited to a very thin layer close to the electrode, the thickness L decreasing with increasing rate of rotation. Outside this layer, the solution is of uniform composition. The concentrations of $\overset{\cdot\cdot}{\mathrm{C}}\mathrm{u}$, for example, at the electrode and in the solution are represented by OC and Bc, respectively. Owing to the circulation of the electrolyte, the concentration in the solution rapidly attains the constant value Bc, and the distribution of concentrations in the layer is given by the line Cc. Now since all the concentrations remain constant during the electrolysis, it is evident that the following relation exists between OC and Bc:

The amount of cupric ion entering the layer in any time is equal to the amount diffusing out into the solution, together with the amount transported in the same time, Or

$$\frac{a\ i\ t}{2 \times 96540} = \frac{D\ S\ t\ (C-c)}{L} + \frac{n\ i\ t}{2 \times 96540}$$

where a = fraction of current used to produce cupric ion,
i = current in amperes,
t = time in seconds,
D = diffusion constant in cms/sec.,
n = transport number of ion in the solution.
Since c = $ait/2 \times 96{,}540\ V$ where V = volume in cc.,

$$C = \frac{a\ i\ t}{2 \times 96540}\left(\frac{1}{V} + \frac{L\ (1-n)}{D\ S\ t}\right)$$

Similar equations hold for the other ions in the solution.

The thickness of the layer was determined by two different methods, and both gave approximately the same result. It was about 6×10^{-4} cms. The diffusion constants were calculated from the mobilities by means of Nernst's formula as modified by Bose. The fall in concentration in the layer was found to be very large. Thus, in one experiment with N/200HCl, the concentration of $\overset{\cdot\cdot}{\mathrm{C}}\mathrm{u}$ at the electrode was 0.8×10^{-8}, while in the solution it was 0.3×10^{-3}. In different experiments, in which the concentrations of HCl, $\ddot{\mathrm{Cu}}$, $\dot{\mathrm{Cu}}$ and CuCl_2' varied, the value of the constant $k_1 = (\ddot{\mathrm{Cu}})/(\dot{\mathrm{Cu}})^2$ was nevertheless very fair, being about 0.3×10^4, instead of 1.4×10^4, as determined by Bodländer and Storbeck.

However, considering the various assumptions on which these calculations have been made, I consider the agreement fair. Experiments are still in progress by which I hope to obtain more accurate results, but the data so far obtained seem to emphasize this point: By the assumption of instantaneous equilibrium at the boundary between anode and solution, the apparently erratic results are reduced to agreement with Faraday's Law.

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